

A UNIFYING PICTURE OF GAS-PHASE FORMATION AND GROWTH OF PAH, SOOT, DIAMOND AND GRAPHITE*

Michael Frenklach

The Pennsylvania State University
University Park, PA 16802

A variety of seemingly different carbon formation processes -- polycyclic aromatic hydrocarbons and diamond in the interstellar medium, soot in hydrocarbon flames, graphite and diamond in plasma-assisted-chemical vapor deposition reactors -- may all have closely related underlying chemical reaction mechanisms. Two distinct mechanisms for gas-phase carbon growth are discussed. At high temperatures it proceeds via the formation of carbon clusters. At lower temperatures it follows a polymerization-type kinetic sequence of chemical reactions of acetylene addition to a radical, and reactivation of the resultant species through H-abstraction by a hydrogen atom.

INTRODUCTION

Carbonaceous solids -- like amorphous carbon, carbon black, soot and graphite -- are known to be structurally related materials (refs. 1-3). They are composed of polycyclic aromatic planes. The arrangement of the planes is what distinguishes these materials: hexagonal crystal lattice in graphite (refs. 2,4) and turbostratic layers of crystallines in soot and carbon blacks (refs. 1,5,6). The turbostratic structures can be transformed into the graphitic lattice with the increase in temperature (ref. 2). Graphite is found to be in equilibrium with diamond at very high pressures, 20 to 80 kbar at temperatures from 1000 to 3000 K (refs. 3,7).

All of these materials can be formed in gas-phase processes at near-atmospheric or lower pressures (refs. 3,5,7-10). It is suggested in this article that the mechanisms of formation and growth under these conditions are closely related to each other. Furthermore, it is suggested that a similar mechanism may be responsible for the formation of polycyclic aromatic hydrocarbons (PAH) and diamonds observed in the interstellar medium (refs. 11-16).

The following discussion is organized in four parts: soot formation in hydrocarbon pyrolysis and oxidation, and the chemical reaction mechanism advanced to explain the observed experimental phenomena; numerical results for the formation of PAH in carbon-rich circumstellar envelopes; mechanism of vapor-deposited diamond; and homogeneous nucleation of diamond at near-atmospheric pressures.

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SOOT IN HYDROCARBON PYROLYSIS AND OXIDATION

Soot production in flame environment has long been a focus of combustion research and a great deal of data have been accumulated. The present knowledge on the global picture of soot formation can be summarized as follows (see references 1,2,5,6,8,17-21 for details). High-temperature gas-phase reactions lead to the production of two-dimensional PAH. These planar molecules then "adhere" to each other forming multi-layered "sandwiches". The PAH planes in these three-dimensional crystallines are arranged without any specific order, and thus they are called turbostratic layers. The crystallines coalesce forming spherical particles, reaching typically an average diameter of 20 to 40 nm, which then agglomerate into chain-like aggregates of the order of 1 μm . In addition to coagulation and agglomeration there is also particle growth due to chemical deposition (of acetylene) on the particle surface, a surface reaction (refs. 22,23). The formation of primary spherical particles takes place on the time scale of a millisecond at flame temperatures, about 1300 to 2000 K (ref. 24).

Of particular interest to the present symposium are the results obtained in high-temperature near-atmospheric hydrocarbon pyrolysis (refs. 25-33), especially those obtained in shock tubes, i.e. under the conditions free of transport phenomena. In the initial work, Graham and co-workers (refs. 25,26) demonstrated that under similar experimental conditions aromatic fuels produce more soot than non-aromatic ones. They also observed that soot yield from aromatic fuels exhibit a bell-like dependence on temperature, i.e., the amount of soot formed increases with temperature, reaches a maximum (at about 1800 K) and then decreases. Further experimental data obtained (refs. 32-35) showed that the bell-like dependence of soot yield on temperature is characteristic of all the hydrocarbon fuels studied. An example of such a dependence obtained for soot formation in pyrolysis of acetylene is shown in figure 1. The soot-yield bell appeared to be a function of reaction time, initial fuel concentration, pressure, absorption wavelength, presence of oxygen, addition of hydrogen, and fuel molecular structure:

- With an increase in reaction time, the soot bell is shifted to lower temperatures with an increase in the absolute yield values (see fig. 1);
- Higher initial fuel concentrations, within the range tested, increase the soot yields with a slight shift to higher temperatures;
- Lowering the total pressure shifts the soot bell to higher temperatures with an increase in the bell width. The effect is more pronounced at lower pressures;
- With changing the probe beam wavelength from the visible to the infrared the soot bell, as determined by light absorption, appears at higher temperatures;
- The addition of small amounts of molecular oxygen shifts the soot bell to lower temperatures. Large amounts of oxygen completely suppress the formation of soot;
- The addition of molecular hydrogen strongly suppresses soot formation (ref. 36); this is demonstrated in Fig. 2.

At very high temperatures, above approximately 2500 K, soot yield begins to increase again, which can be seen in figures 1 and 2 for the pyrolysis of acetylene. This second rise in soot yield is thought to have a mechanism different from that responsible for the soot bell observed at lower temperatures and will be discussed later in the text.

The results obtained in shock-tube experiments were interpreted in light of the following phenomenological description (refs. 32,33). Formation of the first aromatic ring (e.g., phenyl radical or benzene molecule) is the process bottleneck starting with a non-aromatic fuel. Once the aromatic ring is

formed, it reacts with a non-aromatic species (e.g., acetylene molecule or vinyl radical) initiating a polymerization reaction sequence leading to the formation of polycyclic aromatic hydrocarbons. Starting with an aromatic fuel, the process rate is determined by the rate of fragmentation of the aromatic ring. The fragments formed react with the intact rings thus initiating the polymerization sequence of PAH. Addition of oxygen accelerates fuel pyrolysis, which results in a shift of soot formation to lower temperatures; on the other hand, it removes aromatic rings and active intermediates by oxidation, thus suppressing soot formation at high oxygen concentrations (ref. 34).

This phenomenological description was generally supported by the results of detailed chemical kinetic modeling (refs. 36-41). A mechanism of approximately a thousand elementary reversible chemical reactions was generated according to the physical organic chemistry principles. The rate coefficients of these reactions were for the most part estimates. Computer experimentation with the composed mechanism identified the principal reaction pathways leading to the formation of particular stable fused polycyclic aromatics, like acenaphthalene, pyrene, coronene, etc. -- their formation reactions are essentially irreversible and have an effect of pulling chains of reversible reactions. Hydrogen atoms reactivate aromatic molecules to radicals by H-abstraction reactions. The principal reaction pathway for PAH growth in acetylene pyrolysis is depicted in figure 3. As can be seen in this figure, the reaction pathway is essentially a sequence of alternating acetylene additions to aromatic radicals and H-abstractions by hydrogen atoms from forming aromatic molecules.

A detailed analysis of the computational results lead us to conclude that it is superequilibrium of hydrogen atoms which is a driving kinetic force for PAH growth (refs. 37-41). Reactions of class



are highly reversible and the net mass flux through them is determined by the degree of superequilibrium of hydrogen atoms (with respect to the local concentration of molecular hydrogen). Thus, the addition of H_2 decreases the degree of superequilibrium and thus suppresses the growth of PAH. This phenomenon is important for understanding the conditions of PAH growth in the interstellar environment, which is discussed in the next section.

Acetylene addition, following reaction (1), is also a reversible step and, therefore, thermodynamic stability of forming intermediates play an important role in PAH growth. Analysis of this factor (ref. 42) presents arguments against the proposed role of spheroidal carbon clusters in soot particle inception under the conditions of hydrocarbon combustion and pyrolysis suggested by Smalley and co-workers (ref. 43).

The main effects of the presence of oxygen on the polymeric-type growth of PAH were identified to be (ref. 39): (a) promotion of fuel decomposition, which has an effect on the initiation of the reaction route to PAH and soot; (b) additional, rapid production of hydrogen atoms in the initial, small-molecule branching-chain reactions, which drives their concentration above the equilibrium value and thus enhances the polymeric growth of PAH; and (c) oxidation of aromatic radicals by molecular oxygen, which removes them from the polymeric growth process.

An additional factor found to be important in a sooting premixed acetylene flame, i.e. under the conditions of large temperature and concentration gradients, is diffusion of hydrogen atoms from the hot, main reaction zone upstream, into a cooler environment, where they add to acetylene molecules,



thus initiating the formation and growth of PAH (ref. 40).

The reaction pathways to soot in the pyrolysis of individual hydrocarbons other than acetylene were found to relax to the acetylene-addition mechanism initially identified for high-temperature acetylene

pyrolysis (ref. 41). Fuel molecular structure influences the growth process only at its early stages: first, by providing more (or less) efficient reaction partners for the formation of aromatic molecules; and, second, by affecting the generation of hydrogen atoms. Similar behavior was computed for binary hydrocarbon mixtures (ref. 36).

PAH IN THE INTERSTELLAR MEDIUM

There have been recent proposals that previously unidentified near infra-red emission of the Interstellar Medium (ISM) originates from vibrationally excited PAH (refs.11-14,44). It is actually suggested that PAH may be the most abundant organic molecules present in ISM (ref. 45). The question, therefore, is whether PAH can be formed in such large quantities under the conditions of ISM. Applying a general non-homogeneous nucleation theory, Keller recently argued the importance of non-equilibrium factors for the PAH production (ref. 46). The analysis lead him to predict that "A small number of very large PAH's, containing a considerable amount of the condensable carbon" should be produced.

In an attempt to address the question on the grounds of a more rigorous model, Frenklach and Feigelson (ref. 47) investigated gas-phase PAH production under conditions found in dense C-rich circumstellar envelopes, a possible formation site, using the approach of detailed kinetic modeling. The chemical reaction mechanism, initially developed to describe PAH formation in terrestrial flames and discussed in the previous section, was used in the study. The rate coefficients were modified to fit the ranges of temperature and pressure in circumstellar envelopes. The temperature, pressure and velocity gradients were drawn from a number of literature models as well as a grid of constant-velocity-wind models for a parametric sensitivity study.

Starting with a mixture of H, H₂ and C₂H₂, the dominant reaction pathways were found to be sequential acetylene additions and H-abstractions, as in the terrestrial case. Addition of CO reactions did not result in any change. An example of the numerical results obtained for one of the more successful simulations is given in figure 4. As can be seen in this figure, there is no significant PAH production at high temperatures (above 1100 K) and its rate peaks at about 1000 K. This temperature dependence was found to be characteristic to all conditions tested, the peak rate appears within a range of 800 to 1000 K.

The lack of PAH production at high temperatures is the result of high concentration of H₂ in the mixture; and it does not matter much what initial ratio of H to H₂ is assumed -- at the initial temperature of 1600 to 2000 K a partial equilibrium between them is established quickly. In other words, at the high-temperature range of a circumstellar envelope there is no hydrogen atom superequilibrium and hence, as was discussed for the terrestrial case, there is no PAH production. The appearance of measurable quantities of PAH coincides with the growth of H-superequilibrium.

Due to the large hydrogen concentration in the system, both forward and reverse reactions of (1) are fast compared to the acetylene addition reactions. The latter, therefore, are the main "bottleneck" in the PAH production pathway. Since the rate of each of these addition steps is proportional to acetylene concentration, the rate of PAH production becomes strongly, more than linearly, dependent on the initial concentration of acetylene. This dependence on acetylene concentration can be generalized to state that the amount of PAH formed in an circumstellar envelope should depend on the *total* amount of hydrocarbons (or, perhaps, total amount of carbon) present in the wind, since at the initial temperature on the order of 2000 K and the time scale of 10⁸ to 10¹¹ s acetylene is the dominant hydrocarbon species present in the mixture.

Another parameter to which PAH production showed a large sensitivity is the time gas spends at temperatures of about 1100 to about 900 K, while expanding. In other words, PAH production is strongly dependent on wind velocity at the above temperature range and larger amounts of PAH are

computed for very slow winds, with velocities below 1 km/s. For conditions tested, however, even those producing above 1% conversion of acetylene carbon to PAH, the computed average size for PAH distribution is relatively small. This is in disagreement with the prediction of Keller (ref. 46), but in accord with the suggestions of Legér and d'Hendecourt (ref. 45) and Allamandola, Tielens and Barker (refs. 44,48). Further details can be found in reference 47.

LOW-PRESSURE VAPOR-DEPOSITED DIAMOND

Synthetic diamond is known to be formed at extremely high pressures -- at such pressures diamond is the most thermodynamically stable form of carbon (ref. 7). It has been demonstrated in recent years that diamond (and diamond-like carbon) can be also produced at low, near- or sub-atmospheric, pressures when diamond is thermodynamically metastable with respect to graphite (refs. 3,7,9,10). Crystalline diamond is shown to be formed in a number of chemical vapor deposition (CVD) techniques: microwave, RF, DC, and UV created plasmas as well as using hot-filament thermal reactors. Both thin films and single crystals can be grown. A variety of initial hydrocarbons were used, however most results have been reported using methane-hydrogen mixtures. Best quality diamond has been obtained using low concentrations (below 1%) of methane. A major problem is the formation of graphite, which kinetically competes with the production of diamond. The details on the apparatus used and the product analysis can be found in recent reviews, references 7 and 10. The focus of the present discussion is on the mechanism of diamond growth.

Induced plasma or hot filament "activates" gas and the formed "active" species then nucleate and are deposited on the substrate surface (refs. 3,9). The question is what are these critical "active" species and what are the elementary steps responsible for nucleation and surface deposition? Several hypotheses have been recently advanced. Tsuda *et al.* (refs. 49,50), based on their quantum computations, proposed a two-step mechanism assuming CH_3^+ to be the key precursor. In the first step, the (111) plane of the diamond surface is covered by methyl groups via methylene insertion or hydrogen atom abstraction followed by methyl radical addition; then, three neighboring groups created on the (111) plane are spontaneously bound to form the diamond structure following the single attack of a methyl cation and the subsequent loss of three hydrogen molecules. The problem with this mechanism is that it cannot explain diamond growth in ion-free environment, whereas such growth has been observed, for example, in hot-filament apparatus.

Mitsuda *et al.* (ref. 51) monitored ultraviolet emission spectra during synthesis of diamond in a low-pressure microwave plasma reactor with a $\text{CH}_4\text{-H}_2$ mixture. These authors noted that "When the spectra of C_2 radicals were too high as compared with those of CH radicals, graphite was mainly formed. So, C_x radicals were considered to be responsible for the formation of graphite." Similarly, they concluded that " CH_x radicals are related to the diamond formation." However, it is well known that C_2 and CH have extremely high emission efficiencies as compared to those of other radicals and molecules possibly present in the mixture. In fact, C_2 and CH have strongest emission lines in flame spectra (ref. 52), yet it is well established that these radicals do not play any significant role in flame dynamics since their concentrations and hence the associated reaction rates are too low. Analogously, since Mitsuda *et al.* did not determine the absolute concentrations of species they monitor nor they examine other hydrocarbon species present, their conclusions may be circumstantial.

Frenklach and Spear (ref. 53) proposed an elementary-reaction mechanism of diamond growth by a vapor deposition method. The central postulate is that the main monomer growth species is acetylene. The mechanism basically consists of two alternating steps: surface activation by H-abstraction of a hydrogen atom from a surface carbon,



followed by the addition of acetylene. During the addition reaction cycle a number of solid C-C bonds is formed and hydrogen atoms migrate from a lower to an upper surface layer. This mechanism is in general agreement with macroscopic views developed by the Russian school of Derjaguin, Fedoseev and co-workers (refs. 3,9, and cited in 53) and is consistent with major, undisputable experimental evidence:

- a) *Independence on starting material* - Acetylene is produced rapidly in hydrocarbon plasma and high-temperature pyrolysis and is the most abundant gaseous hydrocarbon species present in these harsh environments. Since acetylene is assumed to be the main surface building block, this explains the independence of the growth process from the nature of the hydrocarbon source.
- b) *Hydrogen effect* - Surface reaction (3) is very much similar to its gas-phase counterpart, reaction (1), and, hence, in accordance with the discussion of reaction (1), the net rate of reaction (3) should depend on superequilibrium of hydrogen atoms. The dependence of diamond growth rate on H-superequilibrium was suggested by the Russian researchers based on their experimental findings (ref. 9).
- c) *Co-existence and competition between diamond and graphite growth* - Derjaguin, Fedoseev and co-workers (refs. 9,54) provide a persuasive argument, based on an extensive experimental base, that the growth of diamond and graphite and the close competition between the two are controlled by kinetics. There are two possibilities for the production of graphite along with the growth of diamond: first, formation of graphite precursors in the gas phase followed by surface deposition and further growth and, second, initiation and growth directly on the surface. The gas-phase process would follow the mechanism of PAH formation discussed above. The surface growth of graphite can be envisioned to proceed along similar lines, initiated by structural deviations from the epitaxial growth of diamond (ref. 53). Since the mechanism of diamond growth is also very similar to that of the gas-phase PAH production, the co-existence of the two carbon forms, diamond and graphite, and the specific results obtained under different experimental conditions should be determined by the close kinetic competition between the very similar reaction mechanisms.
- d) *Substrate temperature effect* - The temperature dependence of the rate of diamond growth exhibits a maximum; that is, it initially increases with the substrate temperature and then decreases (refs. 9,55). This phenomenon can be explained as follows. At low temperatures, the growth rate is kinetically limited -- it is controlled by the rate of the H-abstraction, reaction (3), which increases with temperature. As temperature increases, the superequilibrium of hydrogen atoms and the thermodynamic stability of the reaction intermediates both decrease, eventually causing a decline in the growth rate. Graphite formation rates also exhibit a temperature maximum, but at higher temperatures than that of diamond; so are the soot formation rates. Since the intermediates in the growth reaction sequences leading to graphite and soot are more thermodynamically stable than those leading to diamond, the maximum rates of the former should be shifted to higher temperatures compared to that of the latter, as observed in experiment.

The discussed mechanism can also predict some facts of morphology; this and other details can be found in Ref. 53.

INTERSTELLAR DIAMOND

Two recent reports presented evidence that the C δ component of the Allende meteorite is diamond (refs. 15,16). There is a disagreement, however, as to the origin of this diamond. Blake *et al.* (ref.16,

see also reference 56) proposed that "C δ diamond results from high velocity grain-grain collisions behind a supernova shock front in the interstellar medium," whereas Lewis *et al.* (ref. 15) suggested that "part or all of C δ diamond -- not shock-produced but primary, formed by stellar condensation as a metastable phase." One of the arguments of Lewis *et al.* was that diamond is known to be formed in low-pressure CVD processes, as discussed in the previous section; for example, Mitura (ref. 57) reports on gas-phase formation of fine-crystalline diamond powders in an RF plasma. Recent near-atmospheric shock-tube pyrolysis results (ref. 35) may provide additional evidence in support of the "condensation" hypothesis.

As discussed above, soot production in shock-tube pyrolysis of acetylene exhibits a maximum and then a second rise with the increase in temperature (figs. 1 and 2). This second increase coincides with "soot formation" from chloroform and carbon tetrachloride (fig. 2). The product obtained in the pyrolysis of carbon tetrachloride, however, is very different from what is typically known as soot: it looks white (and hence was termed by us as "white soot", see reference 35); on the transmission electron microscope (TEM) appears as shapeless particles with the size on the order of a micrometer; electron diffraction shows a clear single-crystal pattern with an unidentified d-spacing; and the results of the wet oxidation, performed by Freund and co-workers at NASA-Ames Research Center following the procedures used for C δ analysis of reference 16, indicate that a sizable fraction of the "white soot" has chemical resistance similar to that of diamond.

It was proposed (ref. 35) that the mechanism of "white soot" formation is a clustering-type growth. The formation of the interstellar diamond can be explained as follows. At high temperatures, when the aromatic ring is thermodynamically unstable, yet not too high, so that C-C bonds can still exist, dehydrogenated carbon clusters begin to be formed. Some of them may assume the diamond structure. As the gas expands and the temperature decreases to the point where acetylene becomes a dominant gaseous carbon-containing species, the cluster growth switches to an acetylene-addition mechanism, of the type discussed above, producing amorphous and later sootlike carbon. This would explain the findings of Blake *et al.* (ref. 16) that "the C δ diamond is single phase, but surface and interfacial carbon atoms ... impart an 'amorphous' features to some spectral data." Also, since the nucleation of carbon clusters should be slow in mostly atomized environment and the time spent by the gas within the favorable temperature range should be short, the size of the diamond crystallines should be rather small, as indeed reported in references 15 and 16.

SUMMARY

There appear to be two distinct mechanisms of carbon growth in the gas phase. At high temperatures it is clustering, which may be responsible for the presence of diamond particles in carbonaceous meteorites. At lower temperatures the growth follows sequential H-abstraction and acetylene addition. The general pattern of the two-step reaction sequence, although slightly varying in the specific form it takes, appears to be remarkably similar in such seemingly different processes as soot production in hydrocarbon combustion, PAH formation in carbon-rich circumstellar envelopes, and growth of vapor-deposited diamond and graphite films.

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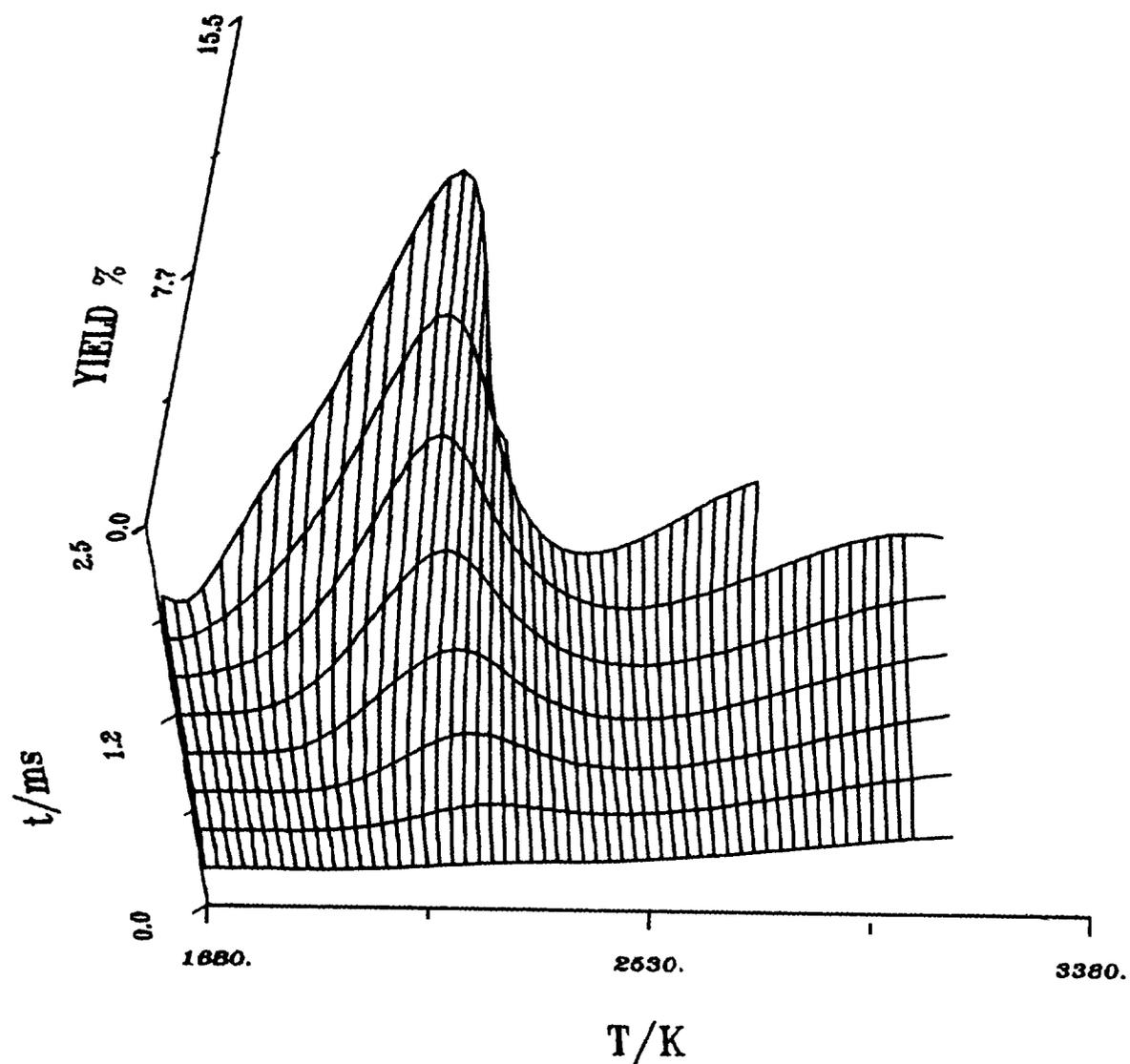


Figure 1.— Soot yield versus temperature and reaction time in shock-tube pyrolysis of a 4.25% acetylene-argon mixture at near-atmospheric pressures; the data are from reference 33, Series D.

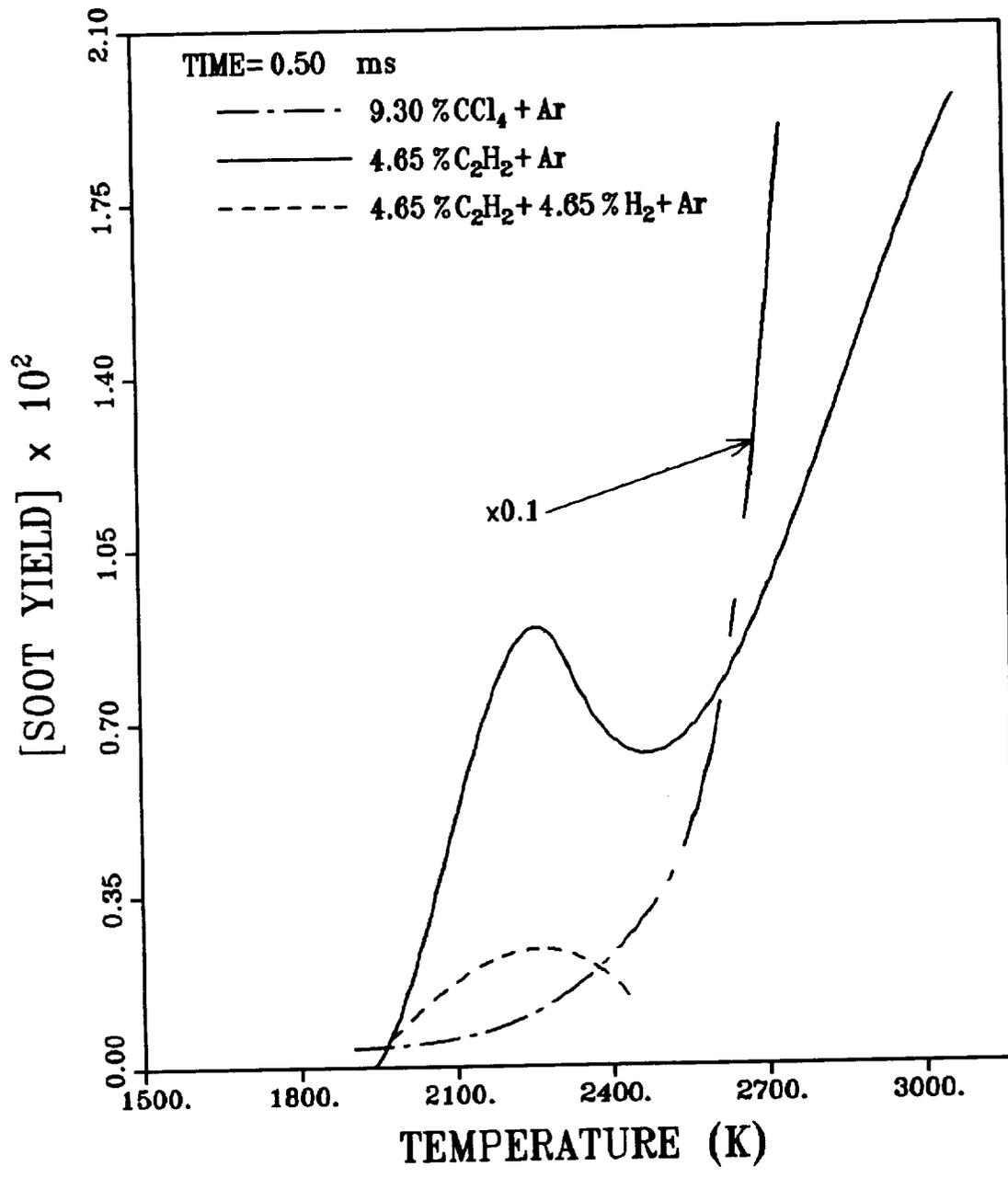


Figure 2.— Soot yields versus temperature in shock-tube pyrolysis of acetylene, acetylene-hydrogen, and carbon tetrachloride argon-diluted mixtures at a reaction time of 0.5 ms; the data are from references 33, 35 and 36.

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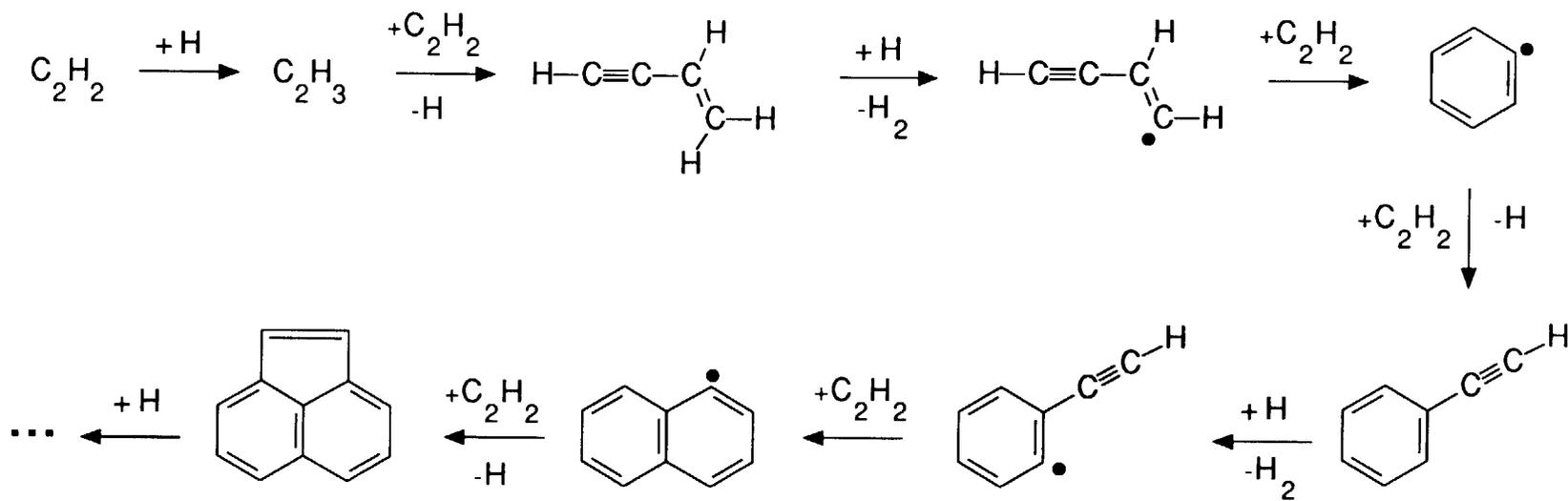


Figure 3.— The dominant reaction pathway for the formation of PAH in acetylene pyrolysis.

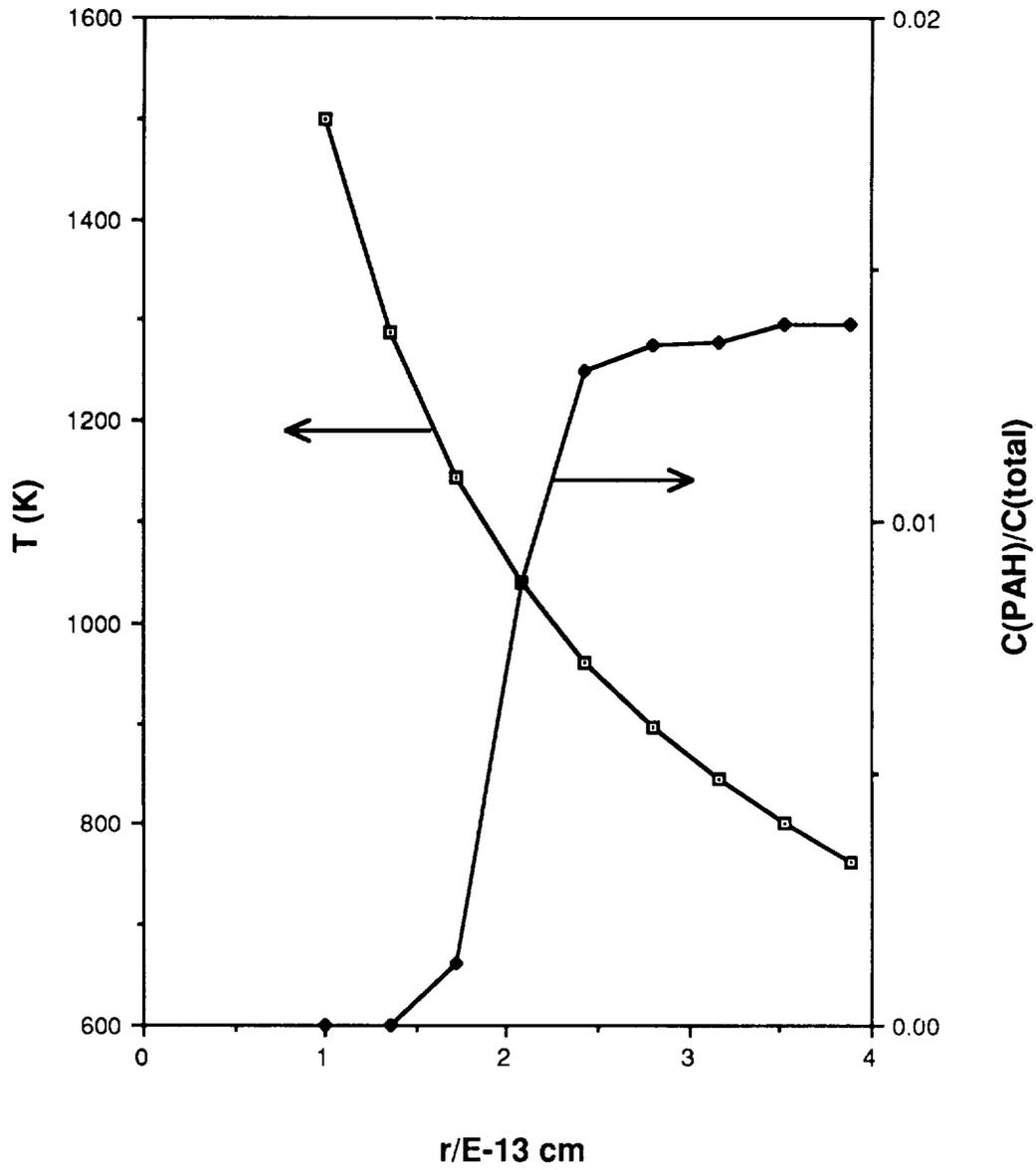


Figure 4.— Computed fractional conversion of acetylene carbon to PAH and assumed temperature profile for a constant-velocity slow wind model: $\dot{M} = 1 \times 10^{-5} M_{\odot}/\text{yr}$; $v = 0.05 \text{ km/s}$; $T = (1500/\text{K}) (r/1 \times 10^{13} \text{ cm})^{-1/2}$; $[C_2H_2]_0 = 0.12\%$; $[H_2]_0 = 99.88\%$

